Electronic Supplementary information (ESI)

Solvent assisted and solvent free orientation of growth of nanoscaled lanthanide sulfides: tuning of morphology and manifestation of photocatalytic behavior †

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[Nd(acda)$_3$(phen)]. Anal. Calcd for $C_{30}H_{32}N_5NdS_6$: C, 45.04 ; H, 4.00 ; N, 8.76. Found: C, 45.38 ; H, 4.22; N, 8.61. IR data (KBr pellet, cm^{-1}): 3356 (m, br), 2940 (s, br), 1604 (s), 1500 (s), 1452, 1311 (m), 1265 (m), 1145 (m), 1098 (m), 1034 (m), 912 (m), 849 (m), 804 (m), 726 (m). ESI-MS(positive) in MeOH: *m/z* 800.25 [Nd(acda)$_3$(phen)H]$^+$ (32%). UV-vis [in *N*,*N*-dimethylformamide, λ_{max}, nm (ε / M^{-1} cm^{-1})] 332 (13088), 384 (29556), 589 (640), 751(110), 807 (156), 878 (47).

[Sm(acda)$_3$(phen)]. Anal. Calcd for $C_{30}H_{32}N_5SmS_6$: C, 44.70 ; H, 3.98 ; N, 8.69. Found: C, 43.97 ; H, 4.08; N, 8.56. IR data (KBr pellet, cm^{-1}): 3353 (m, br), 2938 (s, br), 1607 (s), 1457 (s), 1433 (s), 1095 (m), 1030 (m), 910 (m), 855 (m), 814 (m), 727 (m). ESI-MS(positive) in MeOH: *m/z* 806.35 [Sm(acda)$_3$(phen)H]$^+$ (22%). UV-vis [in *N*,*N*-dimethylformamide, λ_{max}, nm (ε / M^{-1} cm^{-1})] 389 (33227), 333 (16471).

[Tb(acda)$_3$(phen)]. Anal. Calcd for $C_{30}H_{32}N_5TbS_6$: C, 44.23 ; H, 3.93 ; N, 8.60. Found: C, 44.75; H, 3.88; N, 8.63. IR data (KBr pellet, cm^{-1}): 3347 (m, br), 2944 (s, br), 1608 (s), 1500 (s), 1455 (s), 1418 (s), 1267 (m), 1219 (m), 1145 (m), 1102 (m), 1034 (m), 935(m, br), 913 (m), 843 (m), 804 (m), 724 (m). ESI-MS(positive) in MeOH: *m/z* 814.94 [Tb(acda)$_3$(phen)H]$^+$ (18%). UV-vis [in *N*,*N*-dimethylformamide, λ_{max}, nm (ε / M^{-1} cm^{-1})] 387 (33641), 335 (14789).

[Yb(acda)$_3$(phen)]. Anal. Calcd for $C_{30}H_{32}N_5YbS_6$: C, 43.48 ; H, 3.86 ; N, 8.45. Found: C, 44.37 ; H, 3.73; N, 8.56. IR data (KBr pellet, cm^{-1}): 3351 (m, br), 2944 (s, br), 1612 (s), 1461 (s), 1425 (s), 1216 (m), 1105 (m), 1027 (m), 982 (m), 847 (m), 813 (m), 728 (m). ESI-MS(positive) in MeOH: *m/z* 829.04 [Yb(acda)$_3$(phen)H]$^+$ (26%). UV-vis [in *N*,*N*-dimethylformamide, λ_{max}, nm (ε / M^{-1} cm^{-1})] 389 (28567), 330 (11237).

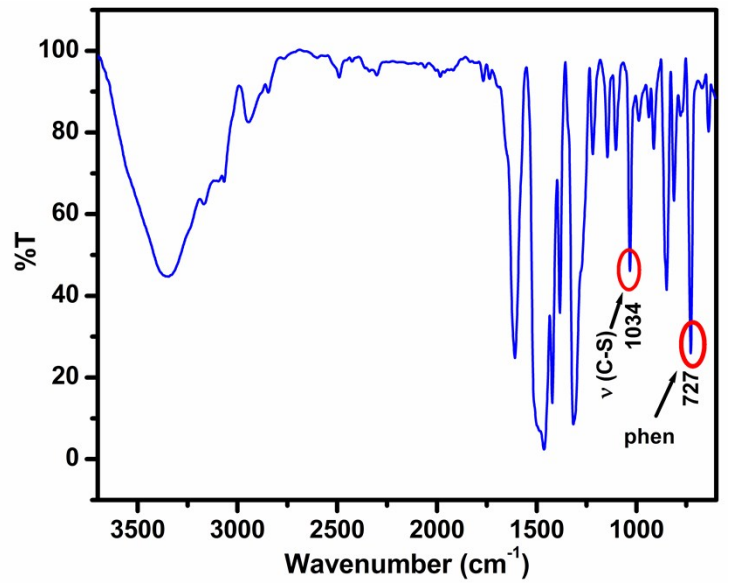


Fig. S1. FTIR spectra of single source precursor complex [Eu(acda)$_3$(phen)].

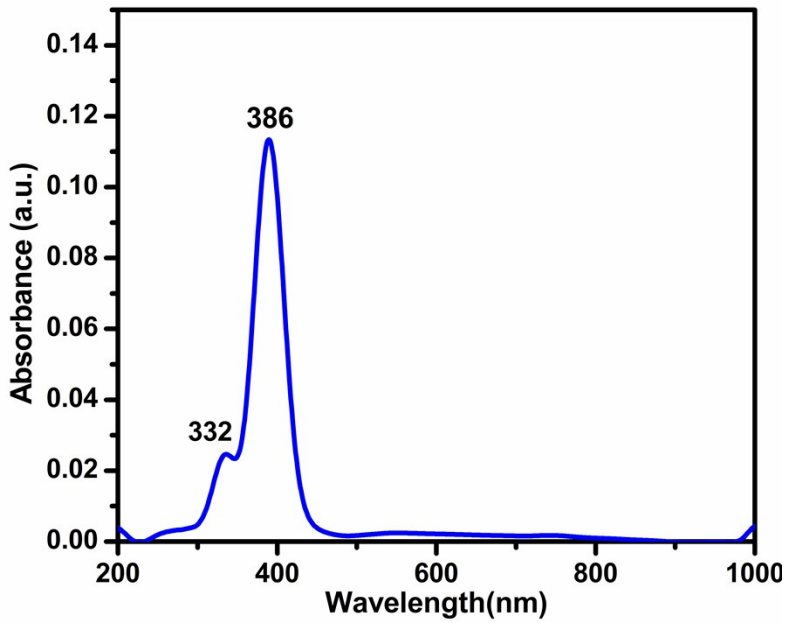


Fig. S2. UV-vis absorption spectra of precursor complex [Eu(acda)$_3$(phen)].

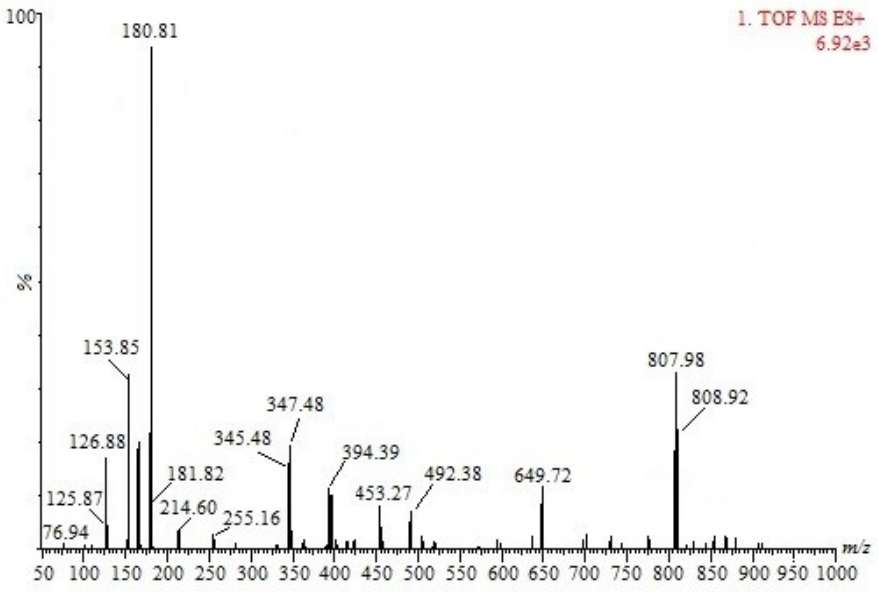


Fig. S3. Mass spectrum of precursor complex [Eu(acda)$_3$(phen)].

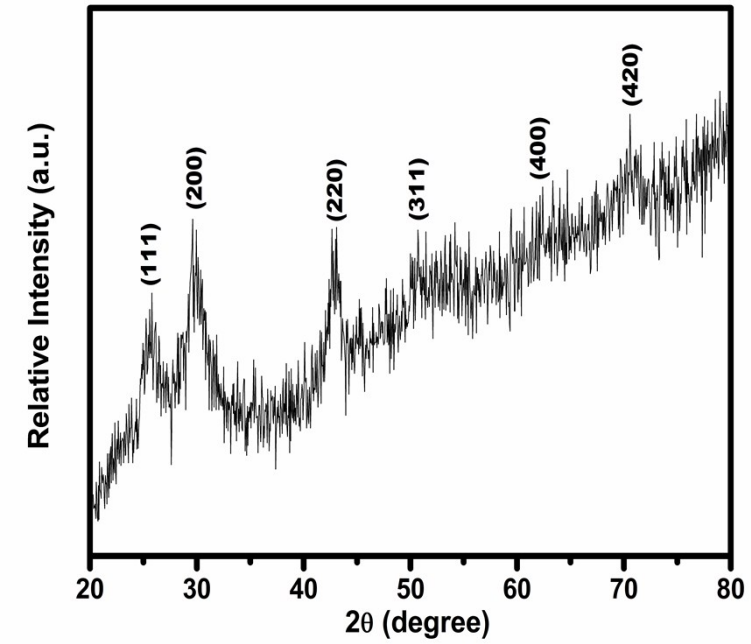


Fig. S4. Powder X-ray diffraction pattern of EuS nanofiber (**2c**)

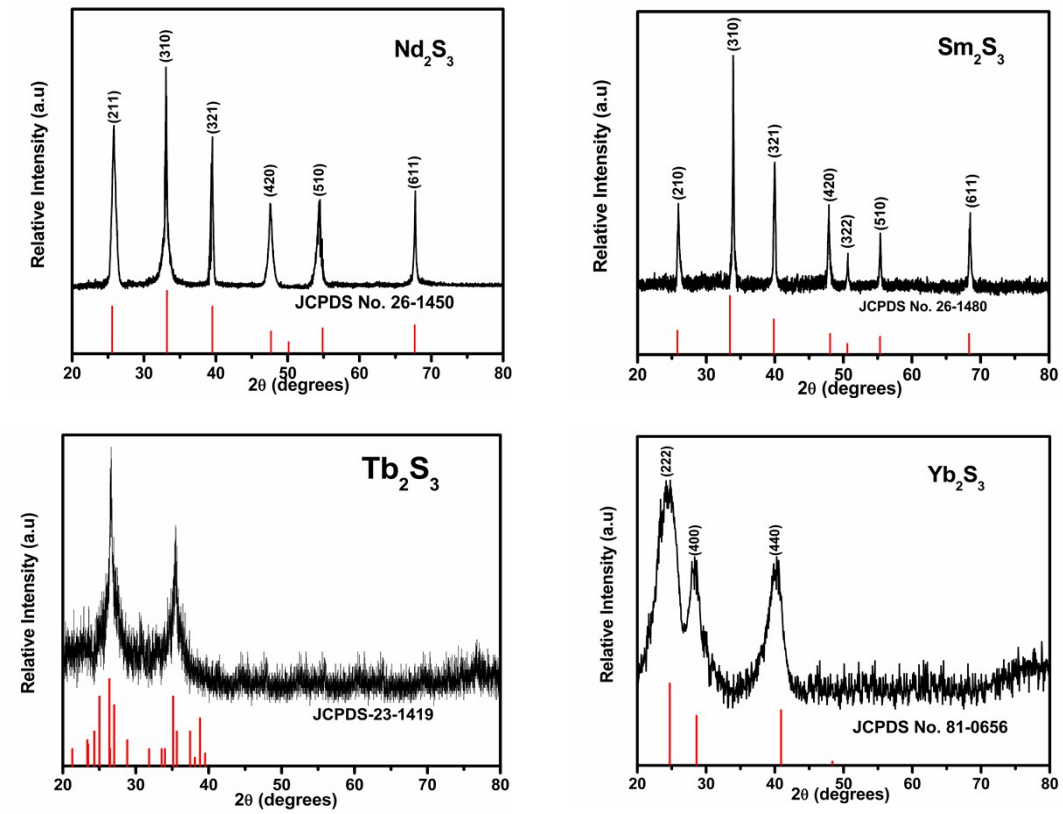


Fig. S5. XRD pattern of Ln_2S_3 synthesised via solid state thermolysis [Ln = Nd, Sm, Tb, Yb]

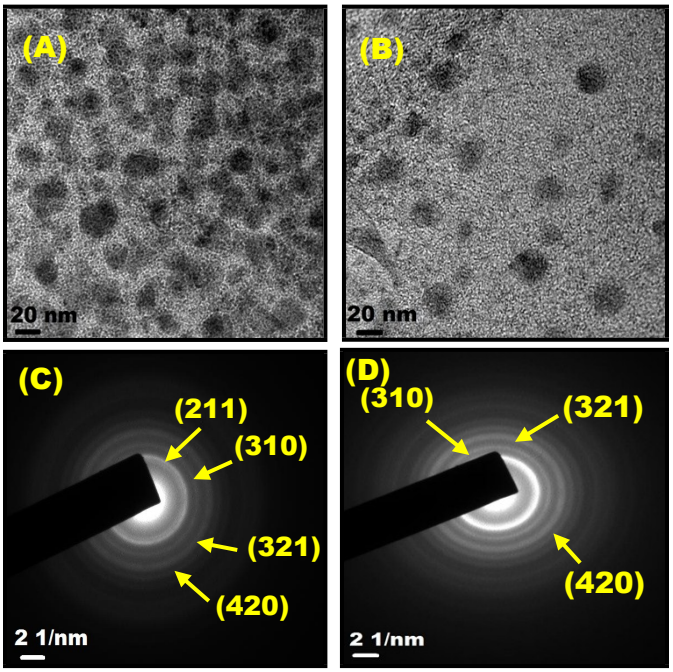
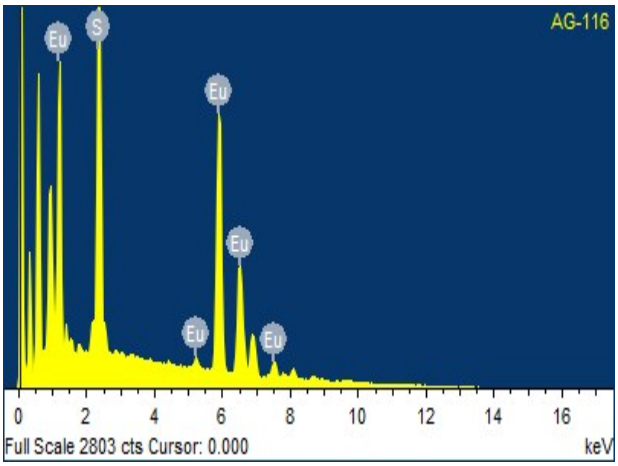


Fig. S6. TEM images and corresponding SAED pattern of (A) and (C) Nd_2S_3 ; (B) and (D) Sm_2S_3 synthesized by solid state thermolysis.



Standard :

S FeS2 1-Jun-1999 12:00 AM

Eu EuF3 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
S K	16.99	49.25
Eu L	83.01	50.75

Fig. S7. Typical EDX pattern of EuS (**2a**) synthesized solvothermally in presence of OAm.

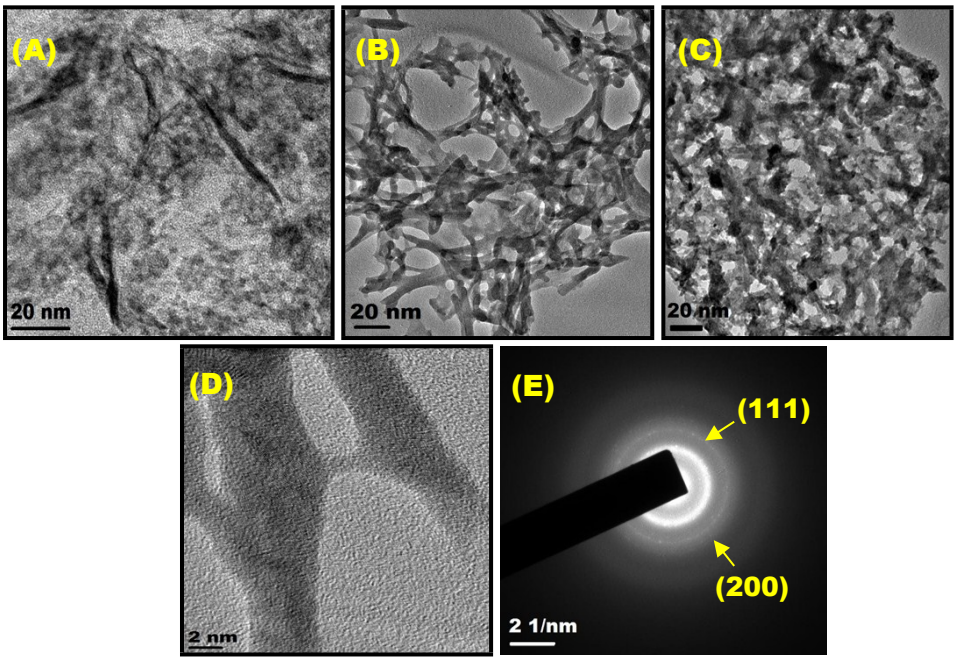


Fig. S8. TEM images EuS (A) (**2d**), (B) (**2e**) and (C) (**2g**). (D) HRTEM images of EuS (**2e**). (E) SAED pattern of EuS (**2e**).

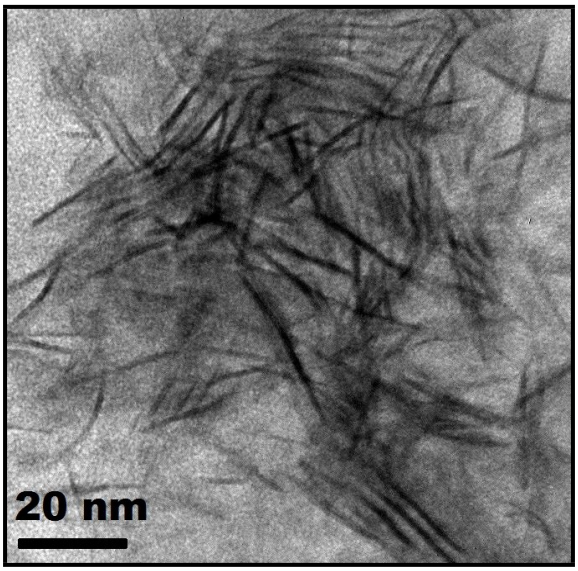


Fig. S9. Typical TEM image of Tb_2S_3 nanofiber synthesized solvothermally in presence of OAm and DDT.

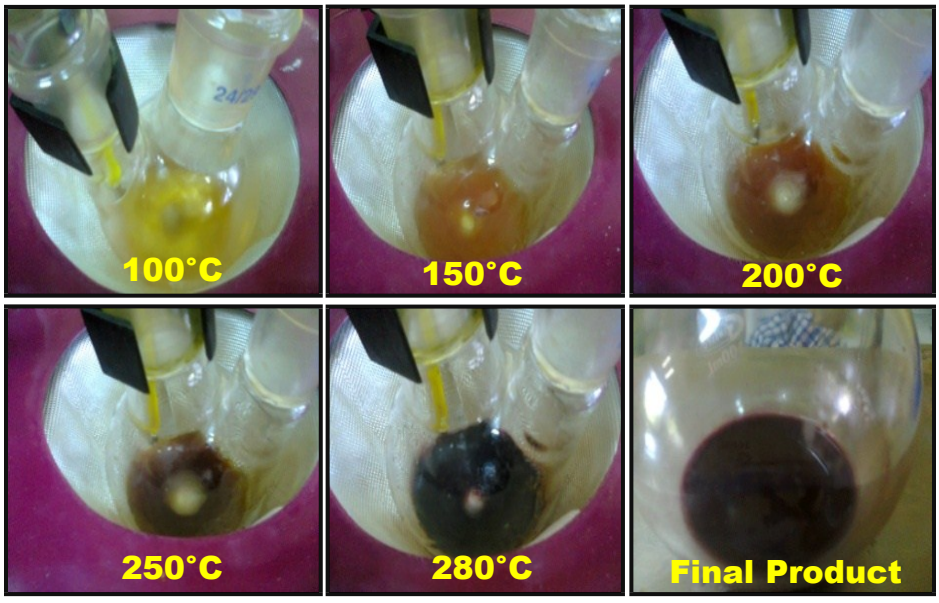


Fig. S10. Formation and colour change of the precursor solution with temperature during the synthesis of EuS (**2a**).

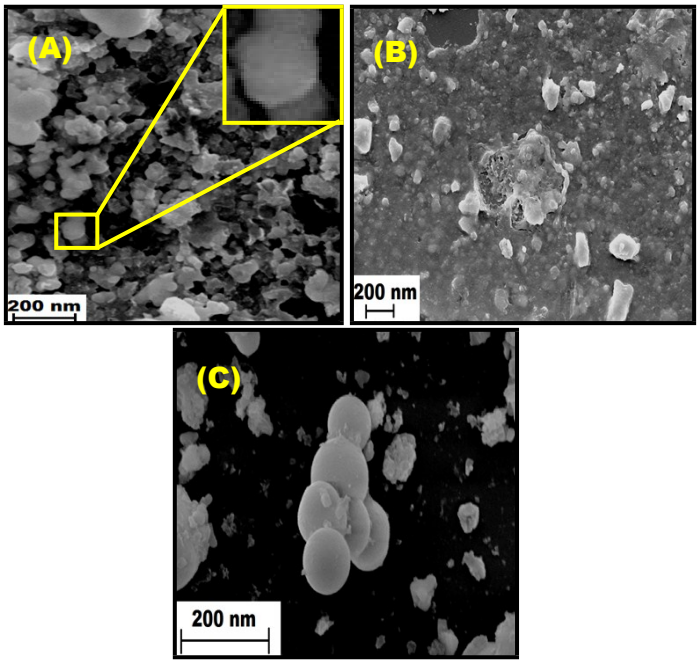


Fig. S11. FESEM images of (A) EuS (**2a**) , (B) EuS (**2b**) (C) Yb_2S_3 synthesized by solid state thermolysis. (A) Inset : magnified view of cube-like orientation.

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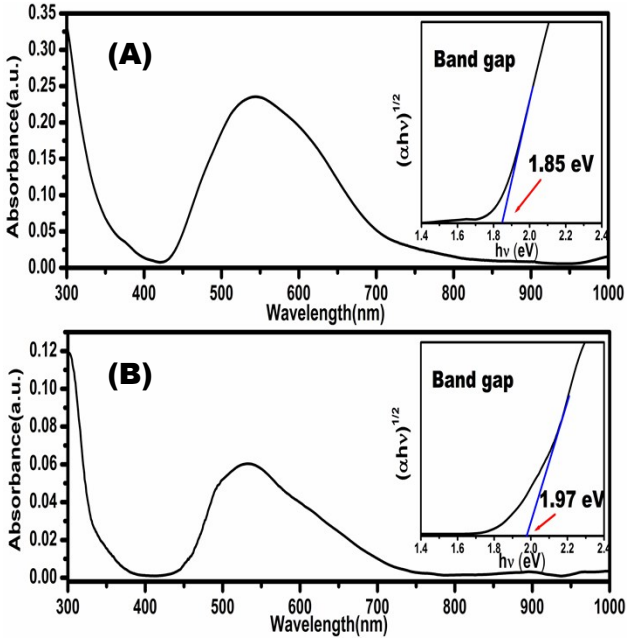

Fig. S12. Uv-vis spectra and corresponding band gap energy calculation for (A) EuS (**2f**), (B) EuS (**2b**).

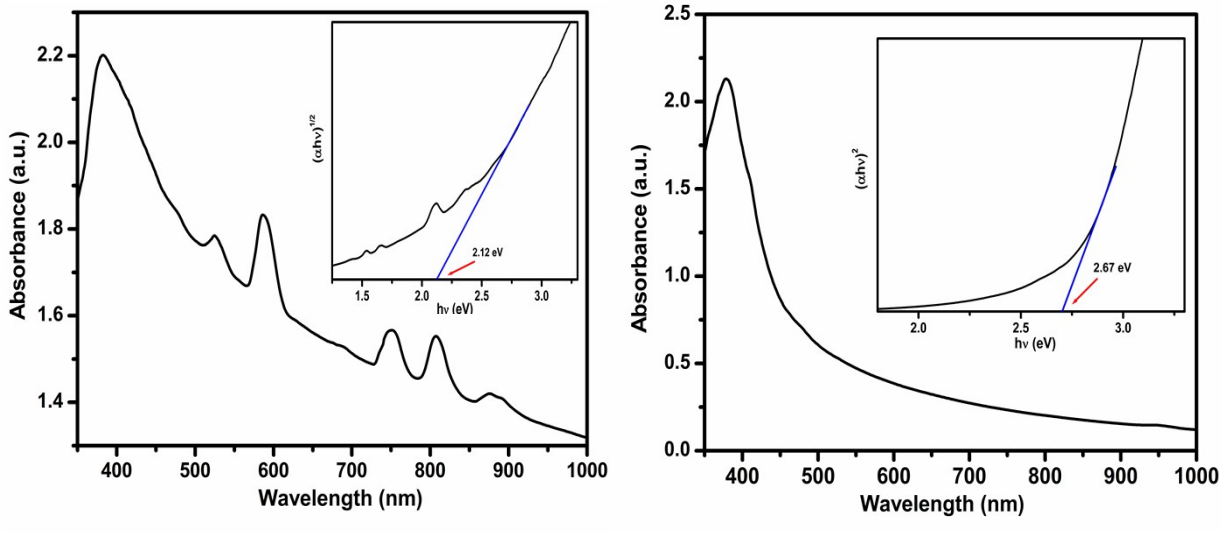

Fig. S13. Uv-vis spectra and corresponding band gap energy calculation for Nd_2S_3 (left panel), Sm_2S_3 (right panel) synthesized by solid state thermolysis.Band gap of Nd_2S_3 and Sm_2S_3 are 2.12 eVand 2.67 eV respectively.

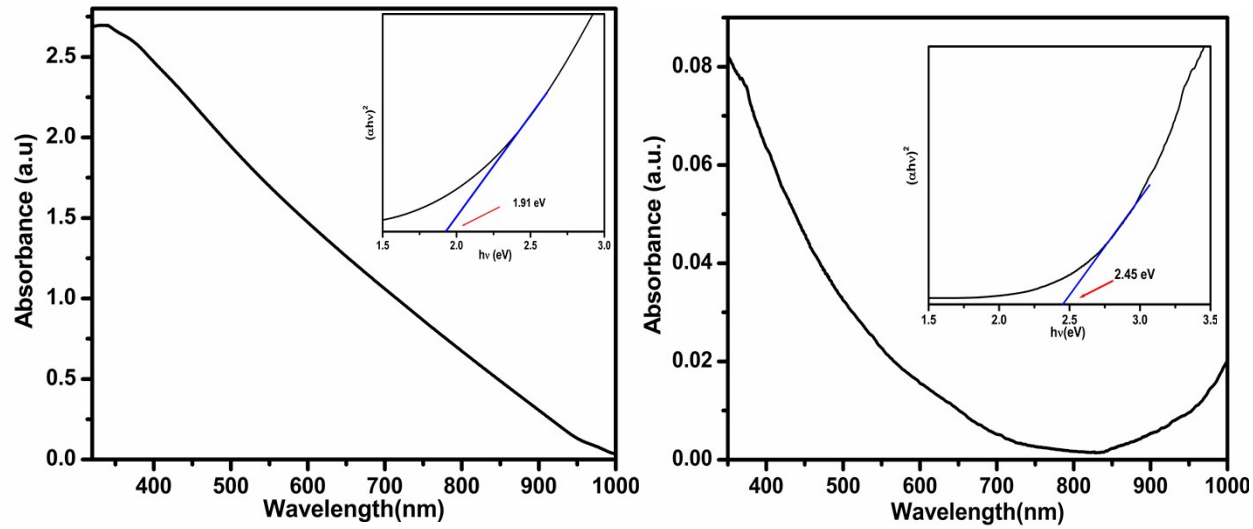

Fig. S14. Uv-vis spectra and corresponding band gap energy calculation for Tb_2S_3 (left panel), Yb_2S_3 (right panel) synthesized by solid state thermolysis. Band gap of Tb_2S_3 and Yb_2S_3 are 1.91 eVand 2.45 eV respectively.

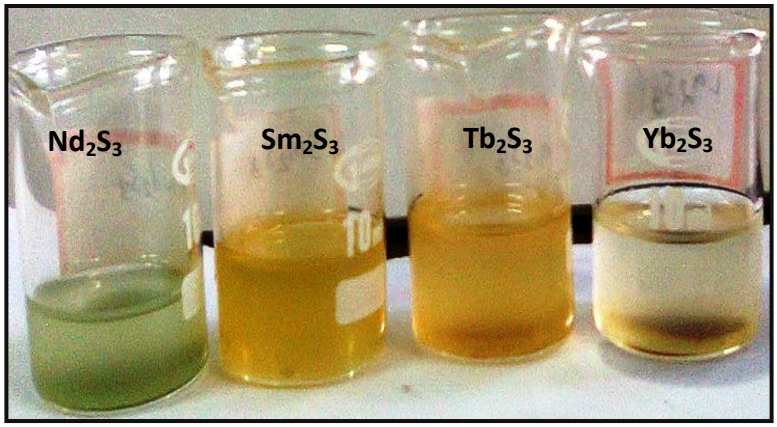

Fig. S15. Colour of the well dispersed solution of Ln_2S_3 (Ln = Nd, Sm, Tb and Yb) in toluene

Table S1. Comparison of morphological features of EuS and corresponding photocatalytic rate constants and half-life values.

Photocatalyst	**Morphology**	**Surface area (m^2/g)**	**Rate constant (RhB) min^{-1}**	**Half life RhB (τ_1)**	**Rate constant (CR) min^{-1}**	**Half life CR (τ_2)**	**Rate constant (MB) min^{-1}**	**Half life MB (τ_3)**
EuS (**1**)	Sphere-like	124.42	3.37×10^{-2}	20.56	2.11×10^{-1}	3.28	3.65×10^{-2}	18.99
EuS (**2a**)	Cube-like	51.14	2.11×10^{-2}	32.84	1.22×10^{-1}	5.68	2.47×10^{-2}	28.05
EuS (**2c**)	Nano-fiber	36.17	1.73×10^{-2}	40.05	1.03×10^{-1}	6.72	1.58×10^{-2}	43.86

Table S2. Comparison of photocatalytic rate constants and half-life values between EuS (**1**) and other lanthanide analogues.

Photocatalyst	Synthetic Method	Rate constant (RhB) min^{-1}	Half life RhB (τ_1)	Rate constant (CR) min^{-1}	Half life CR (τ_2)	Rate constant (MB) min^{-1}	Half life MB (τ_3)
EuS (**1**)	Solid-state thermolysis	3.37×10^{-2}	20.56	2.11×10^{-1}	3.28	3.65×10^{-2}	18.99
Nd_2S_3	Solid-state thermolysis	0.26×10^{-2}	266.54	0.14×10^{-1}	49.50	0.34×10^{-2}	203.82
Sm_2S_3	Solid-state thermolysis	0.08×10^{-2}	866.25	0.17×10^{-1}	40.76	0.14×10^{-2}	495.00
Tb_2S_3	Solid-state thermolysis	0.11×10^{-2}	630.00	0.19×10^{-1}	36.47	0.30×10^{-2}	231.00
Yb_2S_3	Solid-state thermolysis	0.06×10^{-2}	1066.15	0.10×10^{-1}	67.94	0.13×10^{-2}	533.07
TiO_2	Commercially available	0.33×10^{-2}	211.28	0.23×10^{-1}	30.13	0.57×10^{-2}	122.44

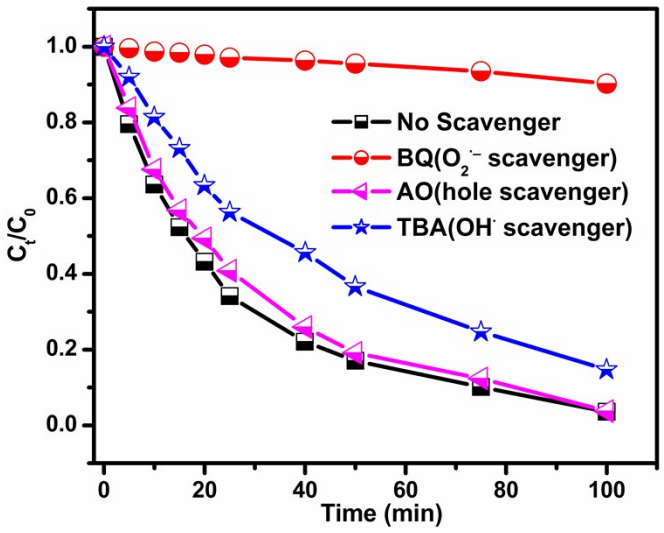

Fig. S16. Time profiles of photocatalytic degradation of RhB with different active species scavengers. (BQ: benzoquinone, AO: ammonium oxalate, TBA: *tert*-butylalcohol)